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"Method for obtaining a thin stabilized, fluorine-doped silica layer, thin layer obtained and application thereof in ophthalmic optics"

The invention relates generally to a process for obtaining a thin stabilized, fluorine-doped silica layer (SiO_xF_y), such a thin layer, and the application thereof in ophthalmic optics, more particularly for obtaining multilayered antireflection coatings for ophthalmic lenses.

Silica-based (SiO_2) thin layers are widely used in optics and more particularly in the field of ophthalmic optics. Such silica-based thin layers are used in particular in antireflection coatings. Such antireflection coatings are conventionally made with a multilayered stacking of inorganic materials. These multilayered antireflection stackings usually comprise one or more layers having a low refractive index which are constituted of a silica-based thin layer.

The deposition techniques for such silica-based thin layers are very diverse, but deposition by evaporation under vacuum is one of the most commonly used techniques. These SiO_2-based thin layers possess very satisfactory mechanical properties and refractive indexes usually of the order of 1.48 for a wavelength around 630 nm.

However, in order to be able to improve the optical performance of the antireflection stacking and to generate novel systems of antireflection stackings, it would be desirable to be able to lower the refractive index of such low index layer while keeping its satisfactory mechanical properties.

In order to solve this technical problem, it has already been proposed to generate porous silica (SiO_2) layers, i.e. in which air has been captured.

Unfortunately, besides complex manufacturing techniques employed, the thus obtained layers possess unsatisfactory mechanical properties which are inferior to those of a conventional silica thin layer.

Moreover, it is known to use fluorine-doped silica thin layers in other technical fields, in particular in the field of microelectronics. In such a case, it is the decrease of the static dielectric constant that is looked for.

The layers are obtained by plasma-assisted chemical vapor phase deposition on silicon wafers.

One of the problems associated with the use of such fluorine-doped silica layers is the alteration of their properties with time.

Patent Application EP 0975017 discloses semi-conductors comprising SiO_2/SiO_xF_y mixed layers coated with a silicon oxynitride layer (SiON), with the aim to prevent fluorine to diffuse outside such mixed layers.

Such Patent Application more particularly describes that depositing a single SiO_2 layer on SiO_2/SiO_xF_y mixed layers does not prevent fluorine to diffuse outside said mixed layer, such a diffusion being likely to occur in the silica layer up to a depth of several hundreds of nanometers.

Obviously, the properties of the fluorine-doped silica layer are thereby altered and adhesion problems may occur at the interface of both layers.

Thus, an object of the present invention is to provide a method for obtaining a SiO_xF_y fluorine-doped silica thin stabilized layer, more particularly having a low refractive index, stable in time and having mechanical properties being at least comparable to prior art layers.

Another object of the invention is to provide a stabilized fluorine-doped silica layer, more particularly as defined hereinabove.

Another object of the invention is to provide a multilayered antireflection coating having at least one low refractive index layer a stabilized fluorine-doped silica layer.

Still another object of the invention is to provide an ophthalmic lens provided with an antireflection coating such as defined hereinabove.

According to the invention, obtaining a stabilized SiO_xF_y layer comprises coating the SiO_xF_y layer with a silica protective layer and/or a metal oxide through an ion beam-assisted vapor phase deposition or through a cathodic sputtering of a metal or silicon layer followed by an oxidation step of said metal or silicon layer.

By ion beam-assistance it is meant bombarding the SiO_2 silica and/or metal oxide layer, during its formation, by a beam of positive ions derived from a rare gas, from oxygen or from a mixture of two or more of such gases.

Examples of metal oxides useful within the framework of the present invention as a material for the protective coating include:

Al_2O_3 (alumina), $BaTiO_3$, BI_2O_3, B_2O_3, CeO_2, Cr_2O_3, Ga_2O_3, GeO_2, Fe_2O_3, HfO_2, In_2O_3, indium-tin oxide, La_2O_3, MgO, Nd_2O_3, Nb_2O_5, Pr_2O_3, Sb_2O_3, Sc_2O_3, SnO_2, Ta_2O_5, TiO, TiO_2, TiO_3, WO_3, Y_2O_3, Yb_2O_3, ZnO, ZrO_2.

The preferred protective layer within the framework of the invention is a silica and/or alumina layer, preferably a SiO_2 silica layer.

Generally speaking, it is recommended to deposit a low thickness of protective layer as well as a relatively low refractive index material, being quite close to the index of the SiO_xF_y layer.

Advantageously, the protective layer is 2 to 40 nm thick, preferably 5 to 30 nm and more preferably, 5 to 20 nm.

If very low thicknesses are being used for the protective layer, it is possible to use a higher index protective layer.

More precisely, if the protective layer has a thickness higher than 15 nm, the index of the protective layer material is preferably lower than 1.65.

If the protective layer is 10 to 15 nm thick, it is possible to use, as the material for the protective layer, a material with an index as high as 2.

However, and generally speaking, it is preferred to use, as a material for the protective layer, a material with an index lower than or equal to 1.65, more preferably lower than or equal to 1.6 and most preferably lower than or equal to 1.55.

In an optimal embodiment of the invention, the index of the protective layer material is lower than or equal to 1.50.

The above-mentioned indexes are refractive indexes at a 550 nm wavelength and at 25°C.

It is quite unique to notice that it is possible to obtain an excellent protection for the SiO_xF_y layer through very low thickness silica and/or metal oxide deposits, generally lower than 40 nm, and typically in the order of 10 nm or less.

Because of the very low thickness of the protective layer, the latter does not detrimentally alter the optical properties of the SiO_xF_y

layer, and it is therefore possible to fully use the low refractive index of the SiO_xF_y layer for obtaining antireflection stackings having an improved performance over that of the prior art.

The gases to be used for the ion assistance are preferably argon, xenon, and oxygen, more preferably, argon and xenon.

The SiO_xF_y silicon oxyfluoride layer can be obtained through any known process.

A method is disclosed in the article «Characteristics of SiO_xF_y Thin Films Prepared by Ion Beam Assisted Deposition (OSA Technical Digest, Optical Interference Coatings, 1998.6), F.J. Lee and C.K. Hwangbo describes in particular the deposition of thin films of SiO_xF_y in a thickness of about 600 nm on glass and silicon substrates. The basic vacuum pressure is 1.2×10^{-4} Pa and the temperature of the substrate is about 150°C. The silicon is evaporated by means of an electron beam in the presence of oxygen in the chamber and the silicon oxide deposit is bombarded during its formation by a beam of polyfluorocarbon ions formed by means of an ion gun starting from CF_4 gas.

A deposition method can also be used with an ion co-assistance. This method consists in evaporating silicon and/or silicon oxide and depositing the evaporated silicon and/or silicon oxide on a substrate surface for forming a layer of silicon oxide, bombarding, during its formation, the silicon oxide layer by a beam of positive ions formed from a polyfluorocarbon compound or a mixture of such compounds and also bombarding the silicon oxide layer, during its formation, by a beam of positive ions formed from a rare gas or a mixture of rare gases.

For forming the silicon oxide layer, a silicon oxide can be used having the formula SiO_x with $x<2$, SiO_2 or a SiO_x/SiO_2 mixture. Preferably, SiO_2 is used. When SiO_x with $x<2$ or a SiO_x/SiO_2 mixture is used, it is necessary that the ambient medium contains oxygen O_2.

The polyfluorocarbon compound may be a linear, branched or cyclic perfluorocarbon compound, preferably a linear or cyclic one.

Linear perfluorocarbon compounds may include CF_4, C_2F_6, C_3F_8 et C_4F_{10}; the cyclic perfluorocarbon compounds may include C_3F_6 and C_4F_8; the preferred linear perfluorocarbon compound is CF_4 and the preferred cyclic compound is C_4F_8.

A mixture of perfluorocarbon compounds may also be used.

The polyfluorocarbon compound may also be a hydrogeno fluorocarbon preferably selected amongst CHF_3, CH_2F_2, $C_2F_4H_2$. The hydrogen fluorocarbon may also be linear, branched or cyclic.

Naturally, a mixture of perfluorocarbon and hydrogenofluorocarbon compounds may be used.

The rare gas is preferably selected from xenon, krypton and mixtures thereof. The preferred rare gas is xenon. If needed, oxygen can be used for providing the co-assistance.

During the deposition of the fluorine-doped silica layer, the substrate is generally at a temperature lower than 150°C, preferably lower than or equal to 120°C and more preferably varies from 30°C to 100°C.

Preferably, the temperature of the substrate varies from 50 to 90°C.

Depositing the SiO_xF_y layer is carried out in a vacuum chamber at a pressure of 10^{-2} to 10^{-3} Pa. If necessary, oxygen gas can be introduced into the vacuum chamber during the deposition of the layer.

Depositing the silicon oxyfluoride layer can be performed by means of cathodic sputtering of a silicon layer followed by an oxidation step of the silicon layer in the presence of a fluorinated gas, for example, by means of an oxygen plasma in the presence of a fluorinated gas such as CF_4.

The method of deposition in a vapor phase is preferred over the cathodic sputtering.

The fluorine-doped silicon oxide layers usually have a thickness of 5 to 300 nm, preferably from 30 to 160 nm, more preferably from 30 to 100 nm.

The resulting fluorine-doped silicon oxide layers have a refractive index n generally ranging from 1.38 to 1.44 (for a radiation of a wavelength $\lambda = 632.8$ nm at 25°C).

Preferably, the deposition of the SiO_xF_y layer occurs without any ion co-assistance.

The layers deposited under ion assistance with rare gases or oxygen generally have therein high stresses, which may be detrimental to

their mechanical properties, and when these are part of a stacking, to the overall properties thereof.

However, in the present case, the very low thicknesses of the protective layer minimize such an effect and it has been observed that the antireflection stackings comprising the SiO_xF_y layer stabilized by the protective layer had quite acceptable mechanical properties which are comparable to the conventional antireflection ones.

The invention therefore also relates to multi-layered antireflection coatings comprising at least one stabilized SiO_xF_y thin layer according to the invention.

The conventional antireflection coatings are made with a mono-layered stacking with a low refractive index (LI) or a multilayered stacking; for example, a high index (HI) / low index (LI) bilayer, (LI/HI/LI) trilayer, (HI/LI/HI/LI) tetralayer, the indexes and thicknesses of which being appropriately selected so as to obtain the antireflection effect, as is known to the person skilled in the art.

Usually, the low index layers are based on SiO_2 silica.

The material with a high refractive index (HI) to be used is a material with a refractive index higher than or equal to 1.55, preferably, higher than or equal to 1.60 and more preferably, higher than or equal to 1.65.

The material with a low refractive index (LI) to be used preferably has a refractive index lower than or equal to 1.52, preferably, lower than or equal to 1.50.

Generally speaking, the refractive indexes being referred to are indexes at a 550 nm wavelength and at 25°C, unless otherwise specified.

The various layers of the antireflection stacking can also be manufactured through cathodic sputtering of a metal or silicon followed by an oxidation step of the metal or the silicon. Using the cathodic sputtering allows with one single device to manufacture all the layers of the stacking and also the SiO_xF_y layer and the SiO_2 or metal oxide protective layer by simply changing the sputtered metal and introducing a fluorine precursor gas in the oxygen during the oxidation step when this is required.

The processes and devices for making the metal oxide and silicon dioxide layers by cathodic sputtering are well known. The Metamode® commercially available process from the OCLI Corporation and the Applied Vision RFX10 sputtering device are to be mentioned.

According to the invention, as the low index layer, a stabilized SiO_xF_y/SiO_2 and/or metal oxide layer is used.

In the case of a multilayered coating comprising two or more low index layers, at least one of the low index layers is made by the SiO_xF_y/SiO_2 and/or metal oxide bilayer according to the invention. Preferably the SiO_xF_y/SiO_2 and/or metal oxide bilayer according to the invention is used for the low index layers in the higher position in the stacking, i.e. the ones being nearest to the air, as this is the case where the antireflection improvements are the most substantial.

In the case of an antireflection coating comprising four HI/LI/HI/LI layers from the substrate surface, the thicknesses of such layers vary preferably in the following respective order, from the substrate surface:

HI: from 10 to 40 nm

LI: from 10 to 55 nm, preferably, from 10 to 45 nm

HI: from 30 to 155 nm, preferably from 40 to 150 nm, and more preferably from 120 to 150 nm

LI (SiO_xF_y layer): from 70 to 110 nm

Protective layer: from 2 to 50 nm.

The antireflection coatings according to the invention can also comprise six layers, in the following respective order, from the substrate surface: HI/LI/HI/LI/HI/LI.

In such a case, the thicknesses of said layers preferably vary in the following respective order, from the substrate surface:

HI: from 10 to 30 nm

BI: from 10 to 55 nm, preferably, from 10 to 45 nm

HI: from 10 to 160 nm

BI: from 10 to 45 nm

HI: from 35 to 170 nm

BI: from 70 to 95 nm

Protective layer: from 2 to 40 nm.

The antireflection coatings according to the invention make it possible to obtain lower reflection coefficients Rm (average of the reflection between 400 and 700 nm) than prior art coatings, with a comparable stacking.

The antireflection coatings according to the invention generally possess a Rm lower than 0.6%, preferably lower than 0.5%, and more preferably lower than or equal to 0.4% (by side of the coated substrate of said antireflection coating).

It is possible to obtain antireflection coatings with a Rm lower than 0.3%.

The definitions of the reflection coefficients (p) at a given wavelength and Rm (average of the reflection between 400 and 700 nm) are known to the person skilled in the art and are mentioned in the standard ISO/WD 8980-4 (specification and method of tests for antireflection coatings).

The SiO_xF_y/SiO_2 and/or metal oxide bilayer according to the invention, as well as the antireflection coatings including such a bilayer, may be deposited on any appropriate substrate, such as silicon, mineral glass or organic glass substrates, for example, organic glass lenses, such substrates being optionally coated with anti-abrasion or anti-shock films, or others as conventionally used.

Naturally, the antireflection coatings according to the invention may comprise coatings adapted to modify their surface properties, such as anti-fouling hydrophobic coatings. These are generally fluorosilane-type materials of a few nanometer thickness.

The remainder of the description refers to the appended figures which respectively represent:

Fig. 1, a schematic view of a device for carrying out the process of the invention;

Fig. 2, a schematic top view of the device of Fig. 1;

Fig. 3, a diagram of the reflection coefficient as a function of the wavelength after depositing the antireflection coatings according to the invention and those commercially available;

Fig. 4, a diagram of the reflection coefficient as a function of the wavelength of an antireflection coating according to the invention and its evolution in time;

Fig. 5, a flow diagram of the Metamode® process applied to depositing a metal oxide layer; and

Fig. 6, a top view of the Applied Vision sputtering device for implementing the Metamode® process.

The device for depositing thin films assisted by an ion beam shown in the Fig. 1 and 2 is a standard device. This device comprises a vacuum chamber 1, the first end 2 of which is connected with one or more vacuum pumps and the other opposite end comprises a door 3. A cold trap 4 may be placed in the chamber close to the end 2 connected with the vacuum pumps. Within the chamber 1 an electron gun 5 is located comprising a crucible 6 adapted to contain the silica to be vaporized. The substrates to be coated A are arranged on a support close to a quartz micro-balance 9. If needed, provision may also be made for an oxygen gas supply to chamber 10. The pressure in the chamber can be measured by means of a hot cathode pressure gauge 8. The supply line 11 of the ion gun 7 is connected with three gas feed drive devices making it possible to simultaneously or independently supply the ion gun with gases of the desired nature and/or flow rates.

In the present case, the vacuum chamber is a Leybold Heraeus chamber adapted to reach a basic vacuum of 5.10^{-5} Pa, the ion gun is a MARK II Commonwealth gun, and the electron gun is a Leybold ESV gun.

For the gas feed drive devices for the ion gun, a BROOKS mass flow control device is used for argon gas, itself controlled by the MARK II control device. For feeding xenon and polyfluorocarbon compound, mass flow control devices are used such as the multigas control device MKS 647 B in which the nature and flow rate of the gases can be programmed.

The same device can also be used for a SiO_xF_y deposition without any ion co-assistance.

The deposition on the substrates of the stabilized fluorine-doped silica layer according to the invention can be carried out in the following manner:

The chamber 1 is placed under a vacuum of 2.10^{-3} Pa (measured by means of the hot cathode gauge 8). The ion gun 7 is initiated with argon gas, then CF_4 gas is introduced (and optionally, a rare gas such as Xe) at the selected flow rate and the argon flow is interrupted (or set at the selected flow rate). The silica (SiO_2) particles located in the crucible 6 are preheated by the electron beam gun. When oxygen gas is used in the chamber 1, it is introduced therein at a controlled flow rate. The electron beam gun 5 and the ion gun 7 are both equipped with a plug, and both plugs of the electron beam gun and the ion gun are opened simultaneously. The thickness of the deposit is regulated by the quartz micro-balance 9 near to the sample substrates When the desired thickness of the SiO_xF_y layer is obtained, both plugs are closed, the emission of the electron beam gun 5 is reduced, Ar or Xe (or O_2) gas is introduced at the selected flow rate in the ion gun 7, then the CF_4 flow is stopped. When the anode voltage and the anode current of the ion gun 7 are stabilized, both plugs are opened, and therefore, a SiO_2 layer is deposited with an ion beam assistance (SiO_2 IAD). When the selected thickness of the SiO_2 IAD layer is obtained, both plugs are closed, the electron beam 5 and ion 7 guns 5 are cut off, the supply of the various gases is stopped, and the vacuum in the chamber 1 is broken.

If an Ar/CF_4 or Xe/CF_4 or O_2/CF_4 mixture is used for depositing the SiO_xF_y layer, when the selected thickness of the SiO_xF_y layer is reached, the CF_4 flow is stopped and the Ar or Xe or O_2 selected flow rate is regulated. In such a way, a SiO_2 IAD layer is deposited. When the selected thickness of the SiO_2 IAD layer is reached, both plugs are closed, the electron beam and ion guns are cut off, the supply of the various gases is stopped, and the vacuum in the chamber 1 is broken.

Naturally, for depositing the SiO_xF_y layer, one may not use an ion co-assistance. In such a case, no rare gas should be introduced into the ion gun 7.

The following examples illustrate the present invention.

By proceeding as previously described, flat surface silicon samples have been coated with fluorine-doped silica layers.

The depositing rate was constant at 0.8 nm/sec.

COMPARATIVE EXAMPLE A

In this comparative example, no protective layer has been deposited. The deposition conditions and the thickness of the SiO_xF_y layer are indicated in the following table.

Deposition Condition for the SiO_xF_y layer

Reference	Thickness SiO_xF_y [nm]	CF_4 flow rate [cm^3/minute]	Anode current [A]	Anode Voltage [V]
Comparative Example A	230	3	0,7	100

EXAMPLES 1 TO 6

CF_4

(CF_4, Ar, Xe in Mark II, O_2 in the enclosure)

Deposition Conditions for the SiO_xF_y layer							Deposition Conditions for the protective layer			
N°	Thickness SiO_xF_y [nm]	Flow rate CF_4 [cm³/min]	Gas flow rate [cm³/min]	O_2 Flow rate[cm³/min]	Anode current [A]	Anode voltage [V]	Barrier layer thickness [nm]	Gas flow rate [cm³/min]	Anode current [A]	Anode voltage [V]
1	185	2,5		4	0,4	100	95	1,8*	0,6	100
2	185	2,5			0,4	100	45	1,5*	0,6	100
3	195	2,5	1,7*	4	1,9	100	10	1,7*	0,6	100
4	190	3			0,7	120	45	1,8*	0,6	100
5	190	2	7⁺		2,8	100	45	6⁺	1	100

*Xe, ⁺Ar

<u>C_2F_6</u>

(C_2F_6 and Xe in Mark II)

N°	Thickness SiO_xF_y [nm]	C_2F_6 Flow rate [cm^3/minute]	Anode current [A]	Anode Voltage [V]	Barrier layer thickness [nm]	Xe Flow rate [cm^3/minute]	Anode current [A]	Anode Voltage [V]
6	210	3	0,7	100	45	0,6	0,6	100

The refractive index has been determined at 25°C for the SiO_xF_y layers obtained for $\lambda = 632$ nm from ellipsometry spectra.

The presence or the absence of water in the SiO_xF_y layer has also been determined through the presence or not of a peak between 3400 and 3600 cm^{-1} in the infrared spectra of such a layer.

The results are presented in the following table :

	Comparative Example A		1		2		3		4		5		6	
Time after deposition	n (SiO_xF_y) @ 632 nm	Presence of water	n (SiO_xF_y) @ 632 nm	Presence of water	n (SiO_xF_y) @ 632 nm	Presence of water	n (SiO_xF_y) @ 632 nm	Presence of water	n (SiO_xF_y) @ 632 nm	Presence of water	n (SiO_xF_y) @ 632 nm	Presence of water	n (SiO_xF_y) @ 632 nm	Presence of water
10 min	1.396	no												
1 hour	1.400			no		no		no		no		no	1.434	no
2 hours	1.403		1.411	no	1.417	no	1.421	no	1.385	no	1.404	no		
3 days	1.440	yes	1.412	no	1.415	no	1.422	no	1.384	no	1.400	no		
1 mo.	1.458	yes			1.418	no	1.421	no	1.383	no	1.394	no		
3,5 mo.													1.432	no
6 mo.			1.404		1.416	no	1.424	no			1.400	no		
8 mo.									1.388	no				

For the unprotected SiO_xF_y layer, the index increases from 1.40 to 1.46 (SiO_2 index) over 1 month, while for the protected layers according to the invention, the index does not change for at least several months.

EXEMPLE 7

The example 7 is an example of an antireflection coating, which can be carried out using the SiO_xF_y/SiO_2 layers of the invention.

The substrate on which such an antireflection coating is produced is an Orma® substrate (diethylene glycol diallylcarbonate based material) coated with an antiabrasion varnish of the epoxysilane hydrolysate type. The antiabrasion varnish to be used has been obtained through pouring dropwise 80.5 parts of HCl 0.1N in a solution containing 224 parts of γ-glycidoxypropyltrimethoxysilane and 120 parts of dimethyldiethoxysilane. The hydrolyzed solution is stirred 24 hours at room temperature, then 718 parts of a 30% colloidal silica in the methanol, 15 parts of aluminium acetylacetonate and 44 parts of éthylcellosolve are added.

A small amount of surfactant is added.

The substrate coated with the varnish is subjected to a 15 minute prebaking step at 60°C, and is then placed in a steaming room at 100°C for 3 hours.

The coating in example 7 is made up of a stacking of layers, starting from the higher layer to the lower layer in contact with the substrate, comprising :

- a SiO_2 IAD layer, being 10 nm thick;
- a SiO_xF_y layer, being 92 nm thick (n=1.42);
- a ZrO2 layer, being 42 nm thick;
- a SiO_2 layer, being 41 nm thick;
- a ZrO2 layer, being 25 nm thick;

Such a coating has a Rm of 0.5 and a Rv (such as defined in the above mentioned ISO WD 8930-4) of 0.4.

The SiO_xF_y and SiO_2 IAD layers (barrier layer) were produced as previously described with the following operating conditions.

Deposition Conditions for the SiO_xF_y layer							Deposition Conditions for the protective layer			
Example	Thickness SiO_xF_y [nm]	CF_4 Flow rate [cm^3/min]	Ar flow rate [cm^3/min]	O_2 Flow rate [cm^3/min]	Anode current [A]	Anode voltage [V]	Barrier layer thickness [nm]	Ar Flow rate [cm^3/min]	Anode current [A]	Anode voltage [V]
7	92	2,0	6		2,2	100	10	6	1	100

The other layers of the stacking are deposited in vapor phase under the conventional conditions as known to the person skilled in the art.

On the antireflection stacking of example 7, a test of «n × 10 strokes» has been conducted. The number of cycles that the stacking can withstand is at least 12.

Fig. 4 is a diagram of the reflection coefficient of the substrate surface as a function of the wavelength , after deposition of the coating of example 7 and of a commercial CRIZAL® antireflection coating formed on an identical substrate.

Fig. 5 is a diagram of the reflection coefficient as a function of the wavelength of the coating of example 7, after deposition, 20 days after the deposition and 3 months after the deposition.

On those figures, the full line curve represents the reflection coefficient as a function of the wavelength of a coating similar to that of example 7, but obtained through modelling according to conventional techniques known to the person skilled in the art.

It can be seen that the antireflection coating according to the invention has an excellent stability in time, comparable to that of conventional coatings.

Descriptions of the measurement methods and tests

n × 10 stroke test

The n × 10 stroke test is described in Patent Application WO/9949097.

Briefly, a fabric is applied to the antireflection treated lens surface and a gum is pressed onto the fabric. The gum and the substrate are then moved one from the other following a back and forth movement. A cycle represents 10 back and forth movements.

The result represents the number of cycles that an antireflection treated lens can withstand before any defect appears.

Refractive index measurement method

Generally, the refractive index is measured through ellipsometry on silicon flat discs.

For the layer in the comparative example A, a SENTECH SE 400 ellipsometer has been used, being calibrated by the SENTECH Corporation.

The measurements are carried out at a wavelength of 632.8 nm at an angle of 70°. The refractive index and the thickness are calculated from tan Ψ and cos Δ by a two-dimensional Newton method, using the following model:

SiOF (n,t)
native SiO_2 (2 nm, n=1.457)
Si (n=3,881, k=0.020)

For the SiO_xF_y layers + protective (barrier) layer, a SOPRA GESP 5 VASE variable angle ellipsometer is used. The device is calibrated according to the procedure as recommended by SOPRA. The tan Ψ and cos Δ spectra between 300 and 850 nm are measured for 3 incident angles 65°, 70° and 75°. With the regression method according to Levenberg-Marquardt, a global adaptation is carried out on 3 spectra using the following model:

SiO_2 (t_1, a_1)
SiOF (t_2, A_2)
native SiO_2
Si

The dispersion curve for Si and for SiO_2 (native) originates from files supplied by SOPRA. For the SiOF and SiO_2 barrier, it is assumed that the dispersion curve obeys a Cauchy law ($n=A+B\lambda^2=C/\lambda^4$, λ en μm), with B=0.003 and C=0.

<u>Characteristic of the flat discs</u>

If {100}, 500 μm thickness, p doped (B), resistivity > 100 Ωcm, two sides polished; (for the IR measurements) 6 samples are cut in a 50 mm ∅ wafer; -->qqs (~3)cm² per sample.

The following examples describe feasible antireflection coatings comprising a SiO_xF_y layer stabilized by the protective layer (in a barrier layer) according to the invention as well as their optical performances.

The optical performance (reflection coefficients) is determined by the FILM STAR DESIGN commercial software from FTG Software Associates – Princetown New Jersey and is indicated hereinafter.

The optical performance of such stackings can also be determined without using the above-mentioned software, through a simple calculation, following the basic principles of the thin layer optics, known to the person skilled in the art and more particularly set forth in the works «Thin film optical filters» Adam Higer Ltd – Bristol 1969 H.A. Mc Loed – Professor of Optical Sciences – University of Arizona – Tuckson.

In the following examples and tables, the layer thicknesses are, unless otherwise specified, indicated in nanometers (nm).

Similarly, unless otherwise specified, the refractive indexes are indexes at 550 nm, 25°C.

The materials being used in the examples are as follows:

Designation of the material	Nature of the material	Refractive index
O	SiOxFy	1.423
N	SiOxFy	1.388
Q	SiO_2	1.473
Z	ZrO_2	1.997
A	Al_2O_3	1.646

EXAMPLES 8 TO 10

The examples 8 to 10 illustrate three antireflection stackings according to the invention, deposited on an ORMA® glass, based on CR39®.

Successively are used as the protective layer, a silica layer, an alumina layer, a zirconia layer, each being 10 nm thick.

The stackings are described starting from the lower layer, in contact with the substrate, up to the higher layer (LI – protective layer).

	Example 8		Example 9		Example 10	
Layer nature	Material	Thickness	Material	Thickness	Material	Thickness
HI	Z	13	Z	13	Z	33
LI	Q	38	Q	38	Q	21
HI	Z	135	Z	135	Z	67
LI	N	82	N	76	N	68
Protective layer	Q	10	A	10	Z	10
Rm (%) stacking	0.21		0.26		0.53	

The above-mentioned table illustrates the fact that it is desirable to use a relatively low index protective layer, more particularly based on SiO_2 in order to obtain the lowest Rm values.

It can however be seen that it is possible to obtain low Rm values (lower than 0.6%), even using a high index barrier layer, as long as the thickness of such a layer is low (10 nm).

EXAMPLES 11 TO 17

Such examples describe antireflection coatings or stackings containing four layers and a protective layer, which is the last layer of the deposition.

		Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17
Layer nature	Material	Thicknesses (layers) [nm]						
HI	Z	40	10	13	14	19	25	26
LI	Q	16	31	45	25	38	39	10
HI	Z	64	126	137	117	150	40	94
LI	O	84	76	82	70	84	94	78
Protective layer	Q	10	10	10	10	10	10	10
Rm (%)		0.5	0.4	0.42	0.49	0.47	0.47	0.45

EXAMPLES 18 TO 24

The examples 18 to 24 illustrate the antireflection stackings of the same type as those described in examples 11 to 17, but using as a low index i.e. layer, the last layer being deposited, a lower index SiO_xF_y layer (N layer).

		Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24
Layer nature	Materia l	Thicknesses (layers) (nm)						
HI	Z	40	10	10	20	12	19	26
LI	Q	18	20	55	37	29	50	10
HI	Z	59	127	136	155	123	30	95
LI	N	86	82	83	85	70	100	78
Protective layer	Q	10	10	10	10	10	10	10
Rm (%)		0.43	0.38	0.46	0.47	0.44	0.44	0.40

EXAMPLES 25 TO 28

In the examples 25 to 28, the thickness of the barrier layer is made to vary.

		Ex. 25	Ex. 26	Ex. 27	Ex. 28
Layer nature	Material	Thicknesses (layers) (nm)			
HI	Z	13	13	13	13
LI	Q	38	38	38	37
HI	Z	134	135	135	135
LI	N	92	82	63	41
Protective layer	Q	2	10	25	45
Rm (%)		0.2	0.21	0.27	0.44

EXAMPLES 29 TO 31

The examples 29 to 31 describe antireflection stackings comprising 6 layers and a protective layer, the last layer of the deposition.

		Ex. 29	Ex. 30	Ex. 31
Layer nature	Material	Thicknesses (layers) (nm)		
HI	Z	16	10	10
LI	Q	33	66	10
HI	Z	157	23	10
LI	Q	17	41	11
HI	Z	150	139	109
LI	O	81	79	78
Protective layer	Q	10	10	10
Rm (%)		0.29	0.40	0.39

As previously indicated, another method for depositing the metal oxide or silicon oxide protective layer as well as the SiO_xF_y layer, is a cathodic spraying deposition or «sputtering» followed by an oxidation step or an oxidation in the presence of a fluorinated gas.

Preferably, depositing the metal oxide or silicon layer occurs carrying out successively the following steps of:

1) depositing a thin metal or silicon layer through cathodic sputtering,

2) oxidizing the resulting thin layer by oxygen, preferably under the form of a reactive plasma,

and repeating such operations as many times as required for obtaining the desired thickness of the protective layer.

Preferably, the deposition 1) and oxidation 2) steps are carried out in two locally distinct processing areas.

The sputtering technique for the thin metal or silicon layer [step 1)] is generally a direct current discharge (dc sputtering) and is carried out under vacuum.

According to this technique, the target, or cathode, made in the material (metal or silicon) to be deposited is supplied by a direct current generator of several kV. The substrate to be coated is placed on an anode, opposite to the target being cooled down through water recycling. After establishing the vacuum, a gas is introduced therein (most often, Argon), and a negative voltage is applied onto the target in order to initiate the

plasma. The positive ions present in the plasma, accelerated towards the target, project the target atoms. The ion impact also causes the ejection of some electron, the so-called secondary electrons, which are accelerated and collide with the gas atoms, allowing to maintain the plasma. The target atoms, once ejected, are deposited on the substrate and thereby create a thin layer.

Other more sophisticated cathodic sputtering techniques are preferred for implementing the invention.

Thus, preferably, a separately supplied anode is used which is not in contact with the substrate.

Preferably still, a magnetron cathode is used. Such cathodes are diode-type cathodes wherein a magnetic field is an electron trap. The electronic currents move in a direction being perpendicular both to the electric field and to the magnetic field according to paths being cycloidal. Thus, they acquire a higher energy, and, more important, travel on much longer distances than in the continuous diode technique. The ionizing collisions are therefore more numerous, hence the densities of the ion current on the target are also higher.

Magnetrons are more particularly described in the works «Handbook of deposition technologies for films and coatings» Science, Technology and Applications, Rointan F. Bunshah 2nd Edition 1994 pp 280-292.

As far as step 2) is concerned, as previously indicated, an oxygen plasma or an oxygen-fluorinated gas mixture is used (for example CF_4). The oxygen plasma dissociates the molecules into oxygen atoms which are very reactive. Creating reactive oxygen atoms enhances the oxidation of the substrate.

An example of a preferred cathodic sputtering method is the Metamode™ method from OCLI, combining all the above described characteristics, and the flow diagram of which is represented in Fig. 5.

Referring to Fig. 5, obtaining a metal oxide layer using the Metamode® method occurs in two distinct chambers, i.e. a cathodic sputtering chamber 1 where the metal from cathode 3 is sputtered onto the lens 4 placed on a tray 5 arranged on a rotating tray 6. Depositing the metal layer occurs as described hereinabove.

Once the metal layer is deposited, through rotating the tray 6, the lens 4 coated with a metal layer is conveyed to the oxidation chamber 2. In said chamber 2, an oxygen plasma is created (or an oxygen and a fluorinated gas, such as CF_4, plasma, if it is desired to obtain an oxyfluoride such as SiO_xF_y) for producing a metal oxide or silicon layer.

The metal/oxidation cathodic sputtering cycle is repeated as many times as needed for obtaining the desired thickness for the final metal oxide or SiO_2 final layer.

As an alternative, the metal cathodic sputtering/oxidation cycle can be repeated modifying the nature of the sputtered metal so as to thereby produce a stacking of metal oxide layers having different natures, for example, in order to produce an antireflection stacking.

The Metamode® method could be implemented with a sputtering device such as the Applied Vision RFX10 apparatus schematically illustrated, in a bottom view, in Fig. 6.

As shown in Fig. 6, the device comprises two cathodic sputtering chambers 1, 2, each provided with an inert gas supply, for example, argon, and a reaction chamber 3, (oxidation or oxyfluorination) provided with a gas supply (oxygen or a mixture of oxygen and a fluorinated gas such as CF_4). The chambers are connected with a vacuum system (not shown in Fig. 6). The substrates to be coated are placed on trays and are supplied to the rotating plate 4 of the device by means of a loading airlock 5. The device further comprises means for monitoring the vacuum 6, such as a Penning gauge, and monitoring and controlling means 7 for the cathodic sputtering and oxidation conditions.

The substrates to be coated, introduced through the loading airlock, are supplied by means of a rotating plate 4 in the cathodic sputtering chamber 1 or 2 where they are coated with a metal or silicon layer, as described hereinabove. After deposition of the metal or the silicon layer, the substrates are supplied into the reaction chamber 3 for carrying out the oxidation or the oxifluorination of the metal or the silicon layer.

At the end of the processing, the coated substrates are unloaded through the airlock 5.

EXAMPLE 32

Silicon flat substrates are coated using the Metamode® method with:

1) a SiOF layer deposited by means of cathodic spraying (sputtering), and

2) a SiO_2 protective layer also deposited by cathodic sputtering.

Deposition condition for the SiOF + barrier SiO_2 layers

Introducing CF_4 occurs through the same gas line as oxygen.

Power on the magnetron with the silicon: 1.5 kW

Plasma gun power (oxygen plasma): 100 W

Deposition of the SiOF layer: (time 900 s; => thickness 165 nm)

Ar flow rate (for Si sputtering): 12 sccm

O_2 flow rate: 4 sccm

CF_4 flow rate: 2 sccm

P: 3 m Torr (0,4 Pa)

Deposition of the barrier layer: (time 90 s; => thickness 15 nm)

Ar flow rate (for Si sputtering): 12 sccm

O_2 flow rate : 4 sccm

CF_4 flow rate: ---

P: 2,6 m Torr (0.35 Pa)

Between both layers the deposition is preferably stopped for ~30 seconds in order to ensure there is no more CF_4 left in the system.

Result: Refractive index of the SiOF layer = 1.415 at 632.8 nm, stable over time.